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MONOTHETIC ANALYSIS OF OCTENE METATHESIS REACTIVE DISTILLATION PROCESS

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ABSTRACT

The monothetic, also known as one-factor-at-a-time, analysis of a reactive distillation process involving octene metathesis to produce heptene and nonene has been carried out in this work. ChemCAD, which is a process simulator, was employed to develop the model of the process while the equilibrium constant of the metathesis reaction occurring in the reaction section of the column was estimated with the aid of Aspen HYSYS via an equilibrium reactor modelling. The input variables considered as the operating factors of the process were reflux ratio, which was varied from 2 to 9, and reboiler duty, which was increased from 0.2 to 0.5 kJ/s with a step increment of 0.1 kJ/s, while the output variables were the mole fractions of heptene and nonene obtained from the top and the bottom sections of the column, respectively. The results obtained from the simulations carried out for the analysis showed that the metathesis reactive distillation process was affected by both the reflux ratio and the reboiler duty of the column. Also discovered from the simulations was that the increase in the reflux ratio made the mole fraction of heptene obtained from the top section of the column to approach one while that of the nonene product given from the bottom section of the column was decreasing. Moreover, it was discovered that increase in the reboiler duty could make the mole fraction of the nonene collected from the bottom section of the column to approach one whereas that of the top heptene was observed to be decreasing. Therefore, it has been revealed from the monothetic analysis of the metathesis reactive distillation process carried out in this study that the quality of the products obtained from the top and the bottom sections of the reactive distillation column were functions of the reflux ratio and the reboiler duty.

Keywords: Olefin metathesis, reactive distillation, monothetic analysis, ChemCAD, Aspen HYSYS.

1. INTRODUCTION

Olefin metathesis can be described as a process of converting an olefin into lower and higher molecular weight olefins. It is a process that belongs to a class of reactions that are suited for integrated process of combining reaction and separation as many of the reactions involved in it are in liquid phase at ambient to moderate conditions, and the reactants and products are similar chemicals. As a result of that, they exhibit very little deviation from Raoult's law. Moreover, the relative order of olefin boiling points in this process is determined based on their molecular weights. So, the boiling points of the products for metathesis reactions straddle the boiling point of the reactant in such a way that the formation of reactive azeotropes is avoided. This allows easy removal of the products, thereby minimizing side reactions and overcoming reaction equilibrium limitations [1-4].

A commercial process for conducting metathesis process using a distillation column [5] was patented by Dow Chemical Company, and it was claimed that reduction of by-product formation and overcoming equilibrium limitations were achieved by carrying out reaction and separation simultaneously, thereby, resulting in increased selectivity and higher yield of the product from the process involving simultaneous reaction and separation over the conventional method of separation following reaction in series [1-4]. This process of accomplishing reaction and separation simultaneously in a single unit piece of equipment is referred to as reactive distillation.

Reactive distillation is a process that combines chemical reaction and multicomponent separation into a single piece of equipment [6-10]. It has been a focus of research in chemical process industries and academia in the last few years [11], and it is a very good alternative to conventional flow sheets with separate pieces of equipment for reaction and separation [12]. This process has been used in a small number of industrial applications for many years, but an increase has been shown in both its research and applications in the last decade [13]. In applying reactive distillation, the reactant and product volatilities must be such that the products can be easily removed and reactants retained inside the column for further reaction. Also, the temperature levels for both reaction and vapour–liquid-equilibrium must overlap [14-23]. By carrying out chemical reaction and separation in one process step as in reactive distillation process, operating and investment costs can be greatly minimized [23-25]. Apart from that, other benefits of this novel process include [26-30]: (i) increased yield, due to overcoming chemical and thermodynamic equilibrium limitations, (ii) improved selectivity via suppression of side reactions, (iii) reduced energy consumption, owing to effective utilization of reaction heat, especially in the case of exothermic reactions, (iv) avoidance of hot spots by simultaneous liquid evaporation, and (v) ability to separate close boiling components. Owing to these advantages, in addition to growing understanding of the process, the chemical process industries have developed an increasing number of processes based on reactive distillation.

Many researches carried out on reactive distillation process are available in the literature. Those involving olefin metathesis process include that of Giwa and Giwa [2] in which the optimum parameters required for the operation of a reactive distillation column used for the production of trans-2-butene and trans-2-hexene were estimated with the aid of Aspen HYSYS model of the process that was developed. Furthermore, Giwa and Giwa [31] used layer-recurrent neural network to model a reactive distillation column in which olefin metathesis process was being accomplished. Giwa and Giwa [3] developed AutoRegressive with eXogenous Inputs (ARX) and AutoRegressive Moving Average with eXogenous Inputs (ARMAX) models for olefin metathesis process that was accomplished with a reactive distillation column. Giwa and Giwa [4] applied Aspen Plus to investigate the effects of feed stage on the purity of the top and the bottom products obtained from a reactive distillation process used to produce trans-2-butene and trans-2-hexene by employing a metathesis reaction involving trans-2-pentene.

From the literature review carried out, it was discovered that the application of a process simulator known as ChemCAD to carry out any study concerning olefin metathesis is very scarce. Therefore, it is aimed in this work to apply ChemCAD to carry out monothetic, otherwise known as one-factor-at-a-time, analysis of a - reactive distillation process used for the production of heptene and nonene from the metathesis reaction of octene.

2. METHODOLOGY

2.1 Modelling and simulation of octene metathesis ChemCAD model

The monothetic analysis of the reactive distillation process used for octene metathesis in this work was carried out with the aid of ChemCAD 7.1.2.9917 [32] by developing the model of the process using the process simulator. Shown in Figure 1 is the developed ChemCAD model of the process.

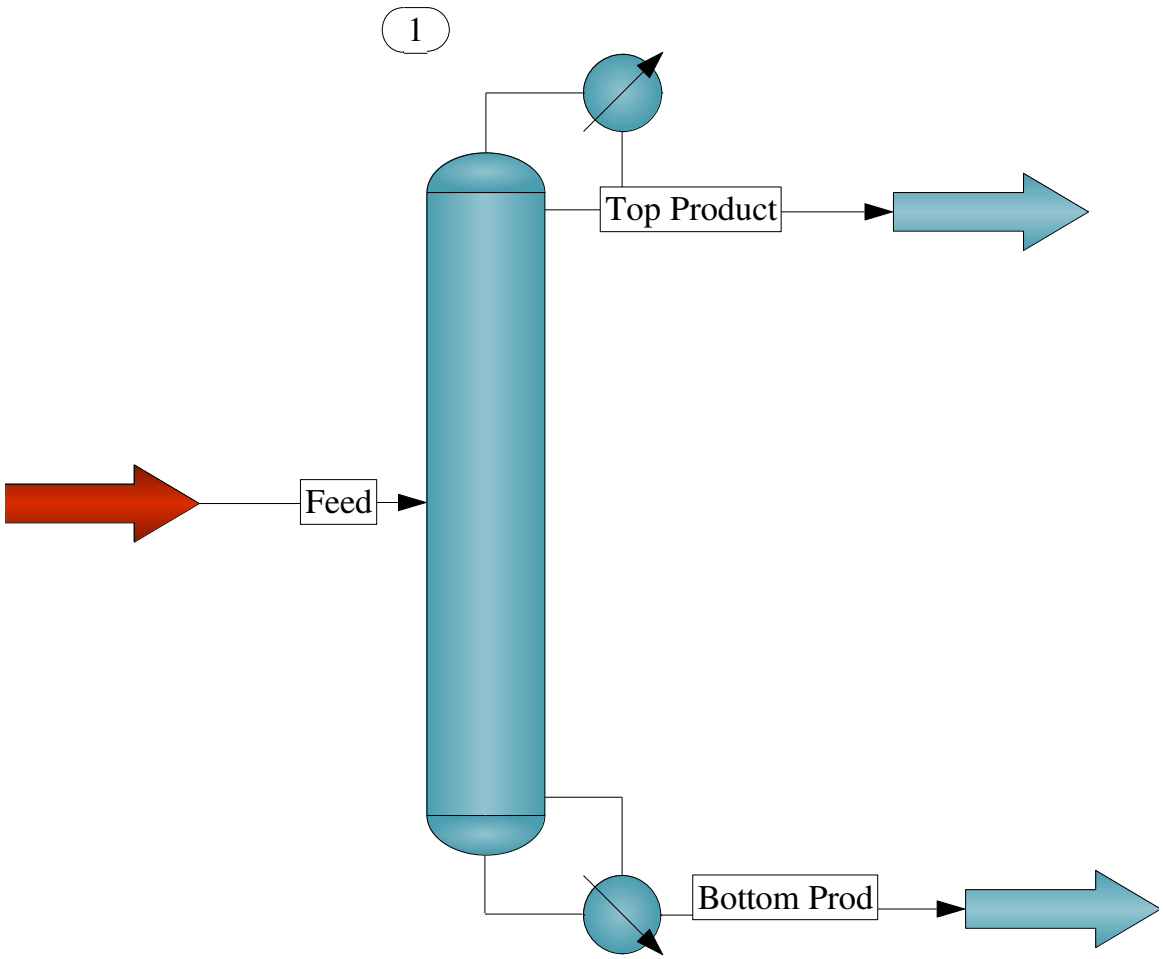

Figure-1. ChemCAD model of the octene metathesis reactive distillation process.

As can be seen from the figure, the model had one feed stream, which was containing octene, flowing at 0.035 L/min and entering the column at a temperature of 25 ^{o}C and a pressure of 1 atm. The column had 21 stages and the feed entered at the 11th stage. Also, the column was divided into five sections, viz. condenser section,

rectifying section, reaction section, stripping section and reboiler section. The reaction section of the column was made to be between the 8th and the 14th stages, in which the metathesis reaction was occurring.

The metathesis reaction occurring in the reaction section of the column, given in Equation (1), was modelled as an equilibrium type whose equilibrium constant was estimated as described in the next subsection. The entire developed process model was simulated using Soave-Redlich-Kwong (SRK) equation of state as the K-value and the enthalpy model with an initial reflux ratio of 2 and a reboiler duty of 0.2 kJ/s before carrying out the monothetic analysis of the process.

$$2C_8H_{16} \xleftrightarrow{K_{eq}} C_7H_{14} + C_9H_{18} \quad (1)$$

2.2 Estimation of Octene metathesis equilibrium reaction constant

The estimation of the equilibrium constant of the octene metathesis reaction was carried out with the aid of Aspen HYSYS [33] model shown in Figure-2. The model also had one feed stream (octene) and two product streams. The feed entered the reactor at s temperature and a pressure of 25 ^{o}C and 1 atm, respectively at a rate of 35 mL/min. Equilibrium reactor was used and the reaction (Equation 1) was modelled in this case also as an equilibrium type, the equilibrium constant of which was set to be estimated using Gibbs Free Energy using the expression given in Equation (2).

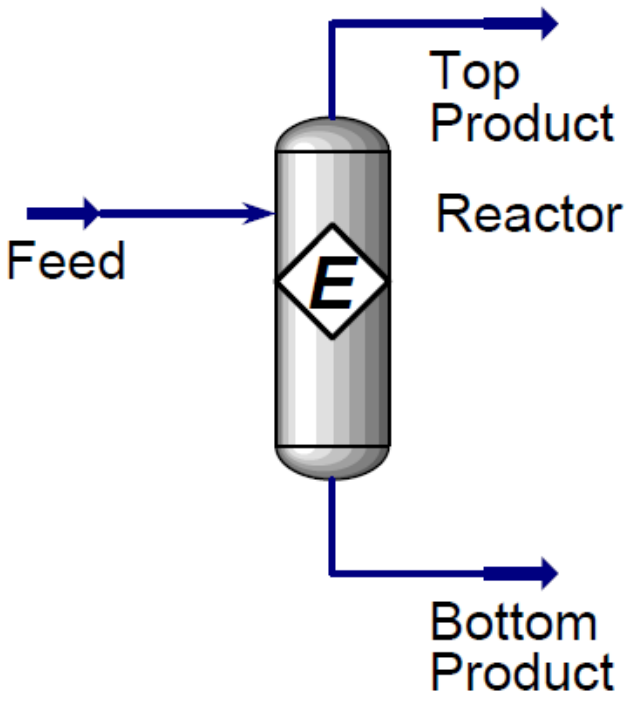

Figure-2. Aspen HYSYS model of octene metathesis for equilibrium constant estimation.

$$\ln(K_{eq}) = -\frac{\Delta G_{reaction}}{RT} \quad (2)$$

where K_{eq} is the equilibrium constant, ΔG is the free energy change, R is the universal gas constant and T is the temperature.

The basis of the equilibrium reaction in Aspen HYSYS simulator was set to activity, and the base component was the only reactant involved, which was octene.

3. RESULTS AND DISCUSSIONS

The equilibrium constant obtained for the process with the aid of Aspen HYSYS was found to be 0.9766 at a conversion of 66.85%. Considering the value of the conversion given by the process, the value of the equilibrium constant was found to be good, and it was adopted in the simulation of the Chem CAD model of the reactive distillation process for octene metathesis.

The temperature profile of the column given by the initial simulation, using a reflux ratio of 2 and a reboiler duty of 0.2 kJ/s,of the reactive distillation process for olefin metathesis is given in Figure-3. From the figure, it was observed that the lowest temperature of the process occurred in the condenser (top) section of the column while the highest temperature was found to occur in the reboiler (bottom) section of the column. These observations were found to be in agreement with the basic principles of operation of a reactive distillation column, and, thus, it was established that the developed ChemCAD model of the olefin metathesis reactive distillation process was a valid one that was working properly in principle. It can be noticed from the result given in Figure-3 that a kind of a transition in the temperature profile was seen at stage 11. This was discovered to be due to the introduction of feed at that particular stage of the column.

Shown in Figure-4 are the composition profiles of the components involved in the process as obtained by the initial simulation with a reflux ratio of 2 and a reboiler duty of 0.2 kJ/s. Based on the information obtained from the figure, approximately pure heptene was obtained at the condenser section of the column as the top product while the nonene obtained from the reboiler section was found not to be very pure. The mole fraction of nonene given out from the condenser section of the column was observed to be approximately0.6226, and this was found to be the highest mole fraction value among those of the components present in the bottom section of the column. Similar transitions observed in the case of temperature profile at stage 11 was also found to occur in this case of the composition profiles of the components, and this was discovered to be evidence that the operation of the developed model of the column was consistent.

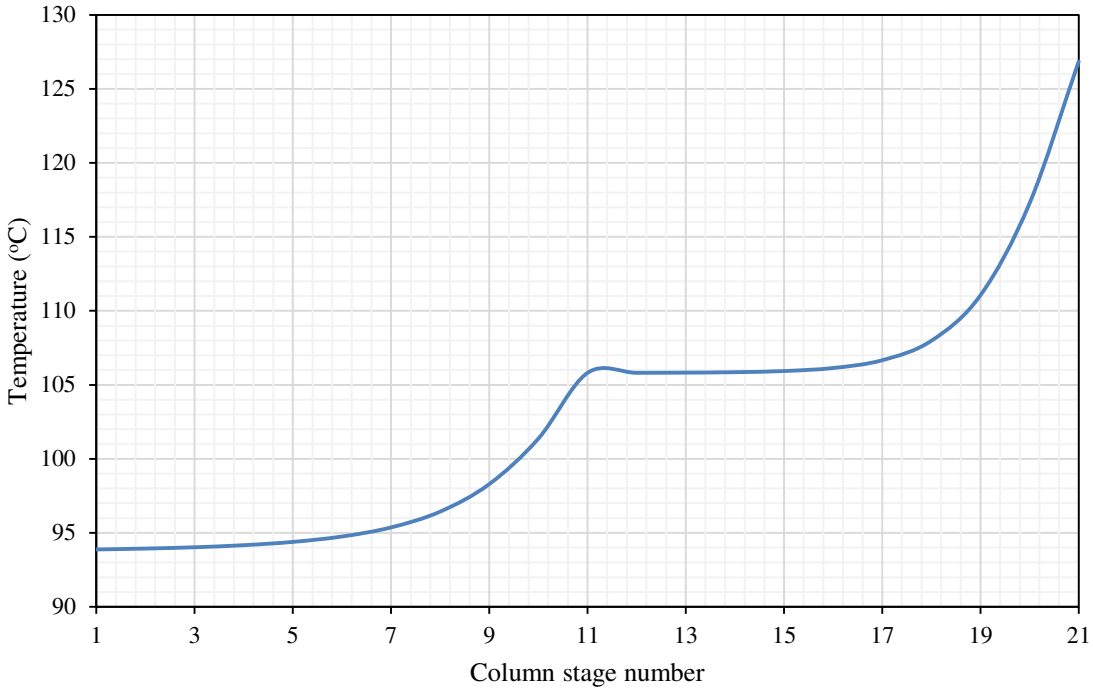

Figure-3. Temperature profile of the column for the initial simulation of the process.

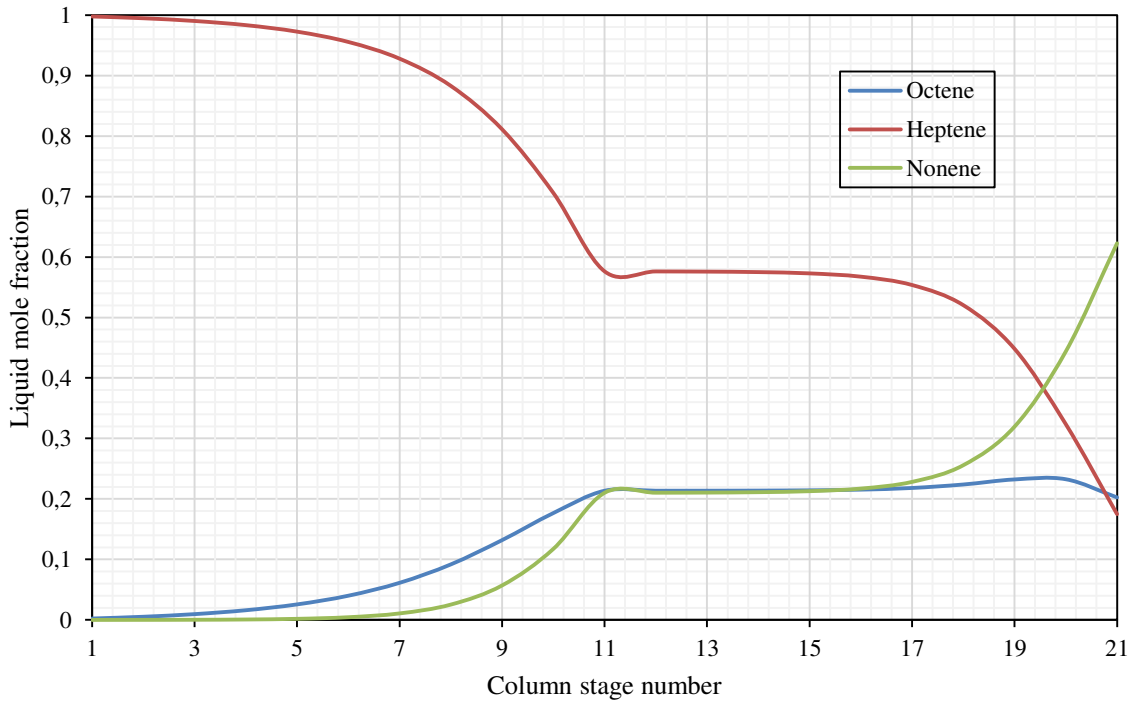

Figure-4. Composition profile of the column for the initial simulation of the process for a reflux ratio of 2 and a reboiler duty of 0.2 kJ/s.

In carrying out the monothetic (one-factor-at-a-time) analysis of the process, the reboiler duty was kept constant at 0.2 kJ/s while the reflux ratio was varied, and the composition profiles were recorded. Given in Figure-5 are the composition profiles obtained when the reflux ratio was changed to 3 while keeping the reboiler duty at 0.2 kJ/s. From the results, it was found out that the mole fraction of heptene obtained from the top section of the column was still approximately one (1) while that of the nonene in the bottom section was found to reduce a little bit from 0.6226 given at reflux ratio of 2 and a reboiler duty of 0.2 kJ/s to 0.5437 at the same reboiler duty but at a

reflux ratio of 3. It has, thus, been seen that the increase in the reflux ratio at constant reboiler duty has resulted in a decrease in the mole fraction of nonene given by the process from the bottom section of the column.

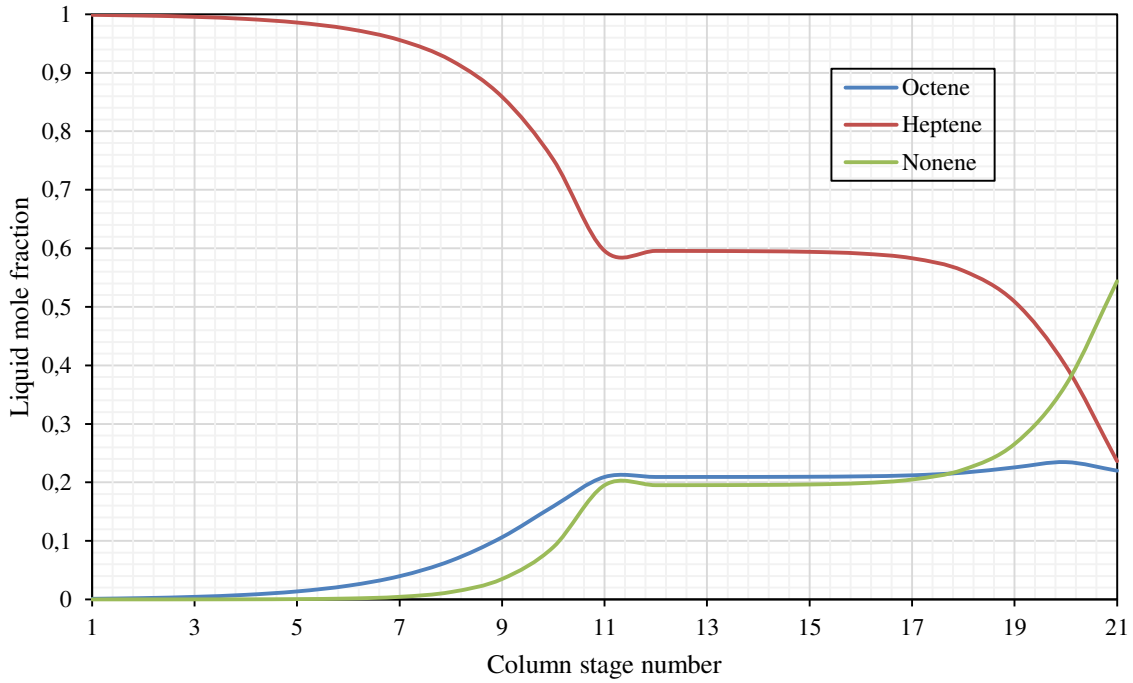

Figure-5. Composition profile of the column for a reflux ratio of 3 and a reboiler duty of 0.2 kJ/s.

Figure-6 shows the composition profile of the simulated process when a reflux ratio of 4 was used with constant reboiler duty of 0.2 kJ/s. It was also noticed from the results given in Figure-6 that the mole fraction of nonene has decreased more than that obtained when the reflux ratio was 3 with reboiler duty of 0.2 kJ/s. In this case of a reflux ratio of 4 and reboiler duty of 0.2 kJ/s, the mole fraction of the heptene given by the process from the top section of the column was still found to be approximately 1.

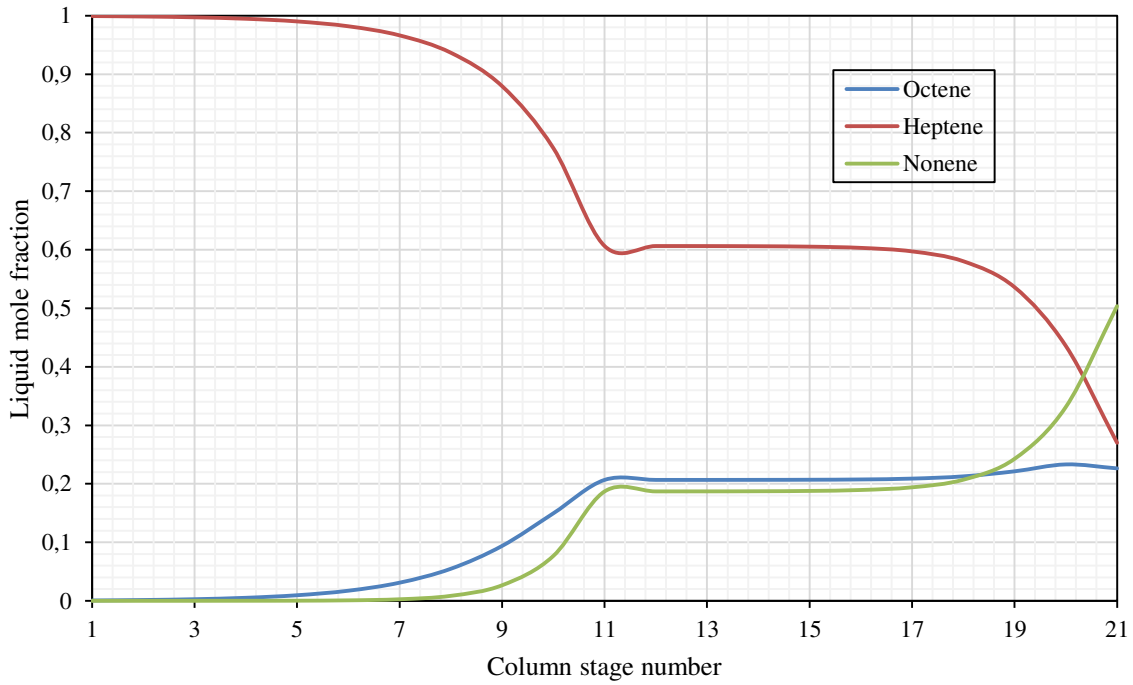

Figure-6. Composition profile of the column for a reflux ratio of 4 and a reboiler duty of 0.2 kJ/s.

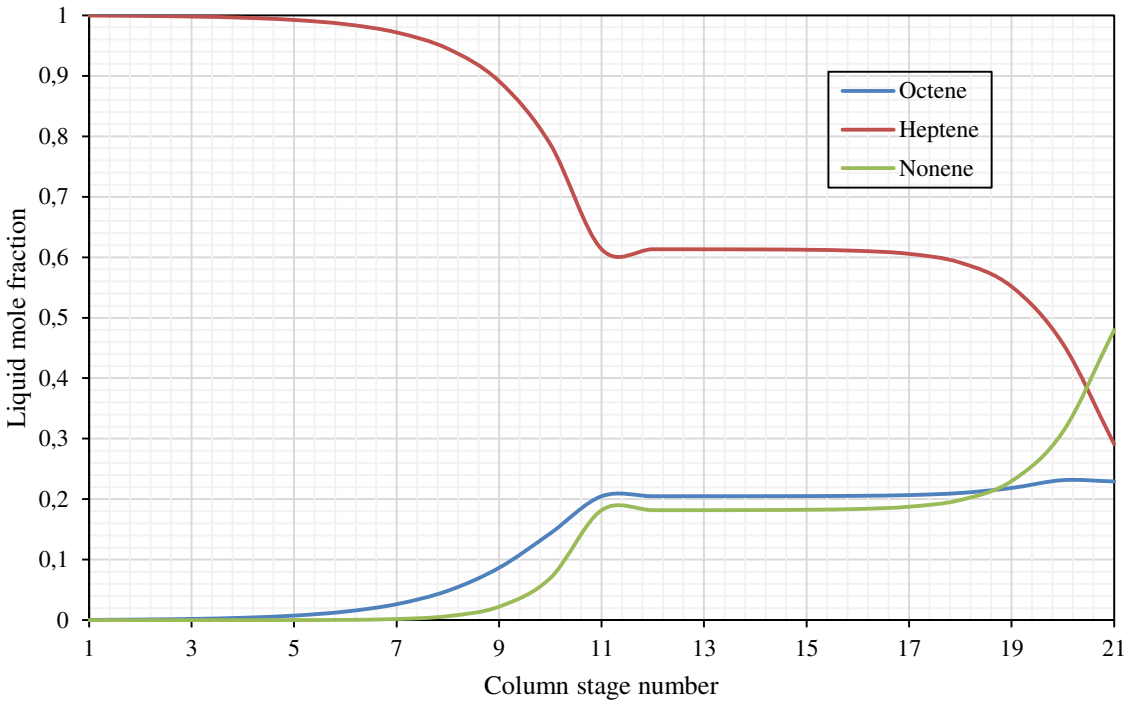

Figure-7. Composition profile of the column for a reflux ratio of 5 and a reboiler duty of 0.2 kJ/s.

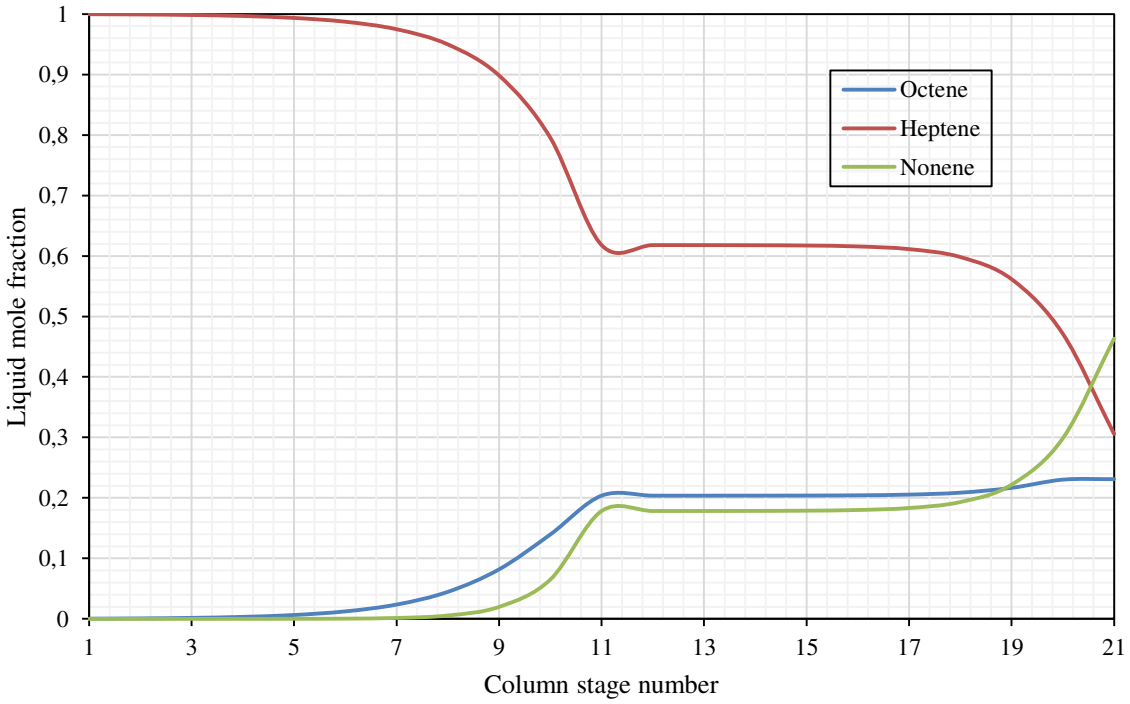

Figure-8. Composition profile of the column for a reflux ratio of 6 and a reboiler duty of 0.2 kJ/s.

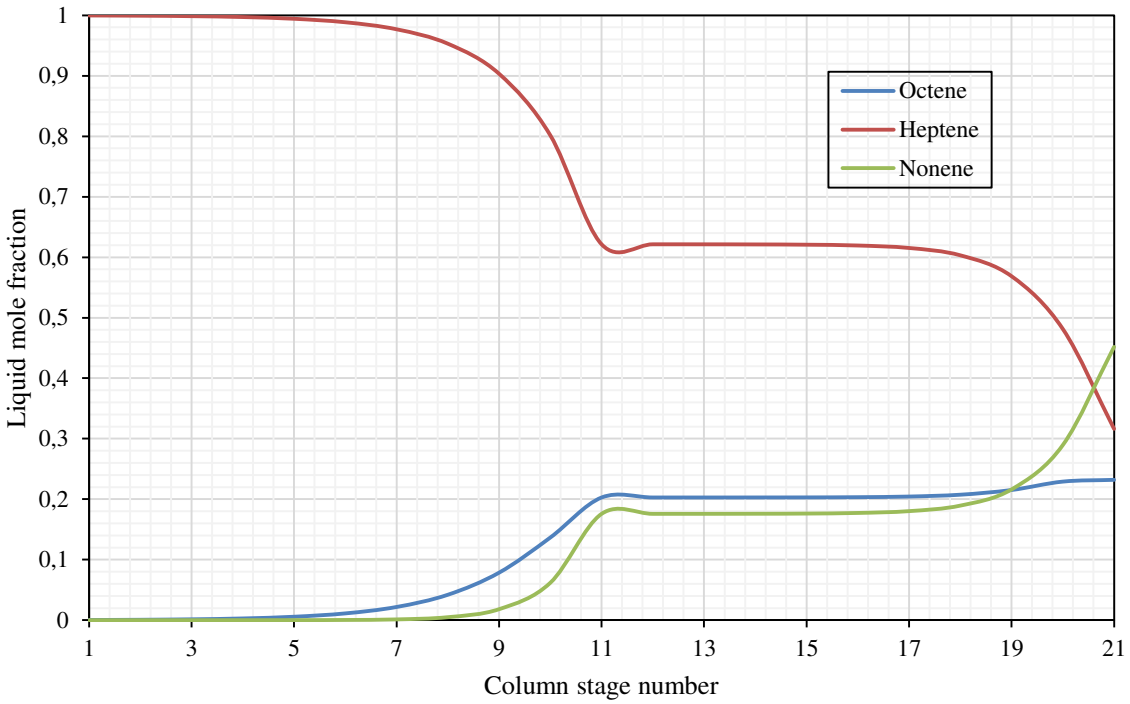

Figure-9. Composition profile of the column for a reflux ratio of 7 and a reboiler duty of 0.2 kJ/s.

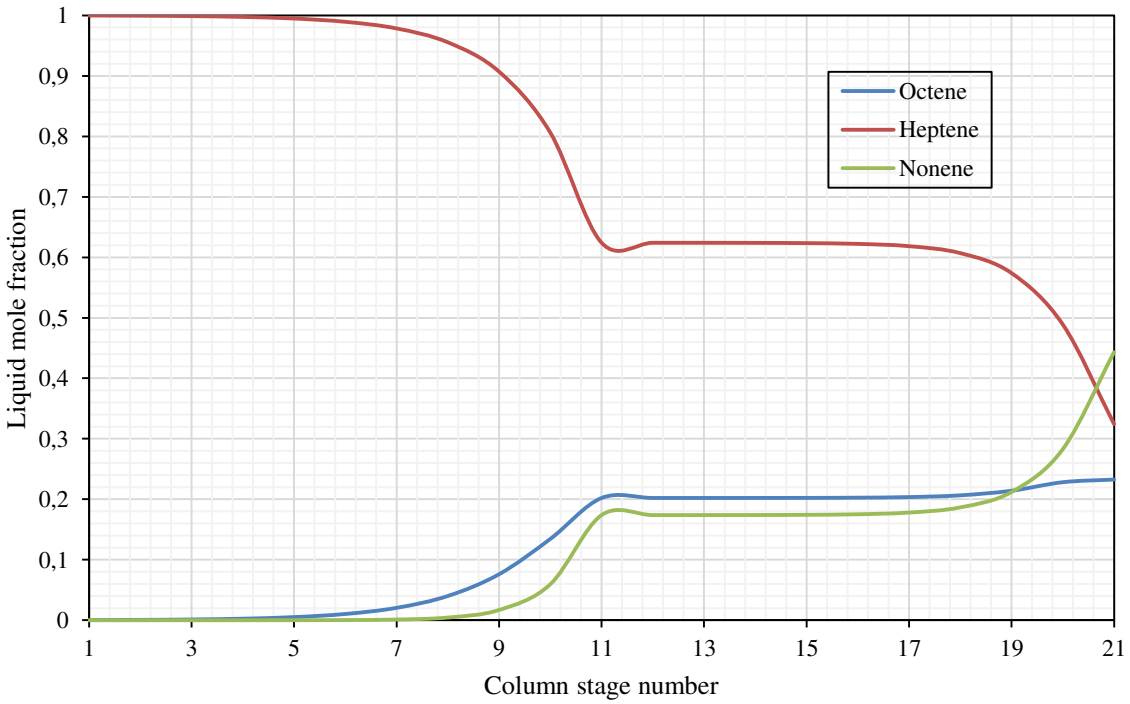

Figure-10. Composition profile of the column for a reflux ratio of 8 and a reboiler duty of 0.2 kJ/s.

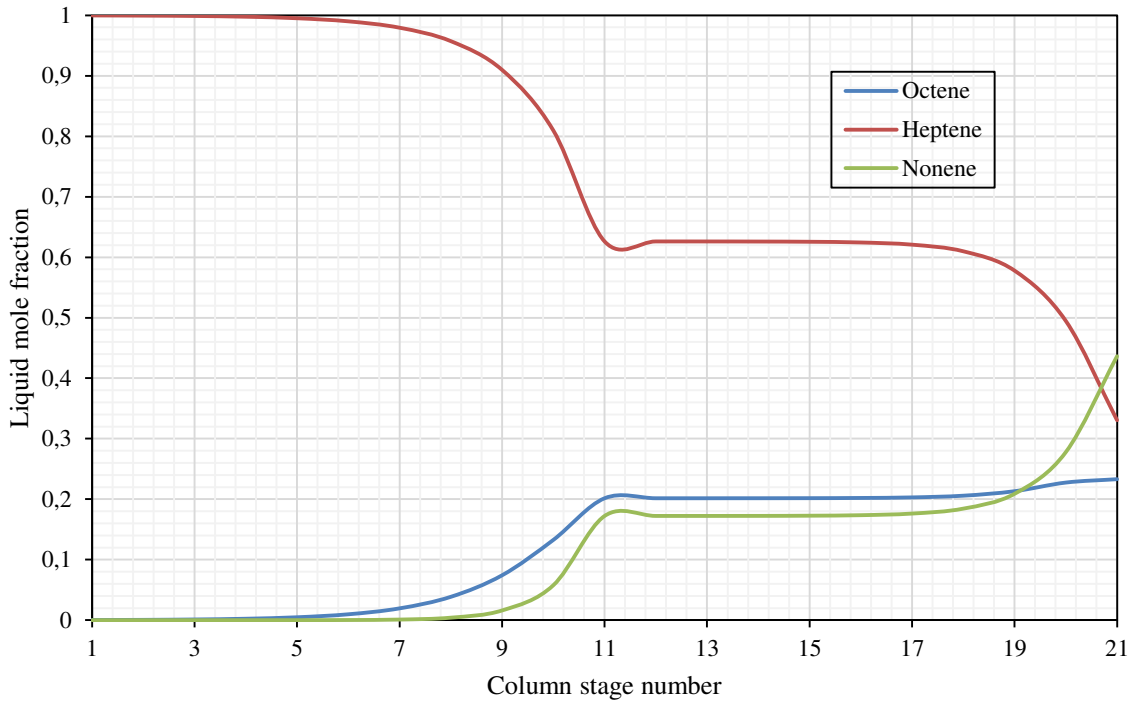

Figure-11. Composition profile of the column for a reflux ratio of 9 and a reboiler duty of 0.2 kJ/s.

Given in Figures 7, 8, 9, 10 and 11 are the composition profiles of the reactive distillation process that was simulated for olefin metathesis using a constant reboiler duty of 0.2 kJ/s and reflux ratios of 5, 6, 7, 8 and 9 respectively. It was observed from the results that as the reflux ratio was increasing while the reboiler duty was kept constant, the mole fraction of nonene given through the bottom section of the column was decreasing and that of the heptene obtained from the top section of the column was still approximately 1.

After studying behaviour of the octene metathesis reactive distillation process with respect to variation in reflux ratio at constant reboiler duty, the reboiler duty was then varied and the response of the system was recorded in each case.

Figure-12 gives the composition profiles of the components involved in the process when the reboiler duty was changed to 0.3 kJ/s with the reflux ratio kept at 2. According to the results shown in the Figure, nonene was found to possess the highest the mole fraction value of very close to 1 in the bottom section of the column. Also observed from the results given in Figure-12 was that the mole fraction of heptene obtained from the top section of the column had decreased when compared with its value obtained with a reflux ratio of 2 and a reboiler duty of 0.2 kJ/s.

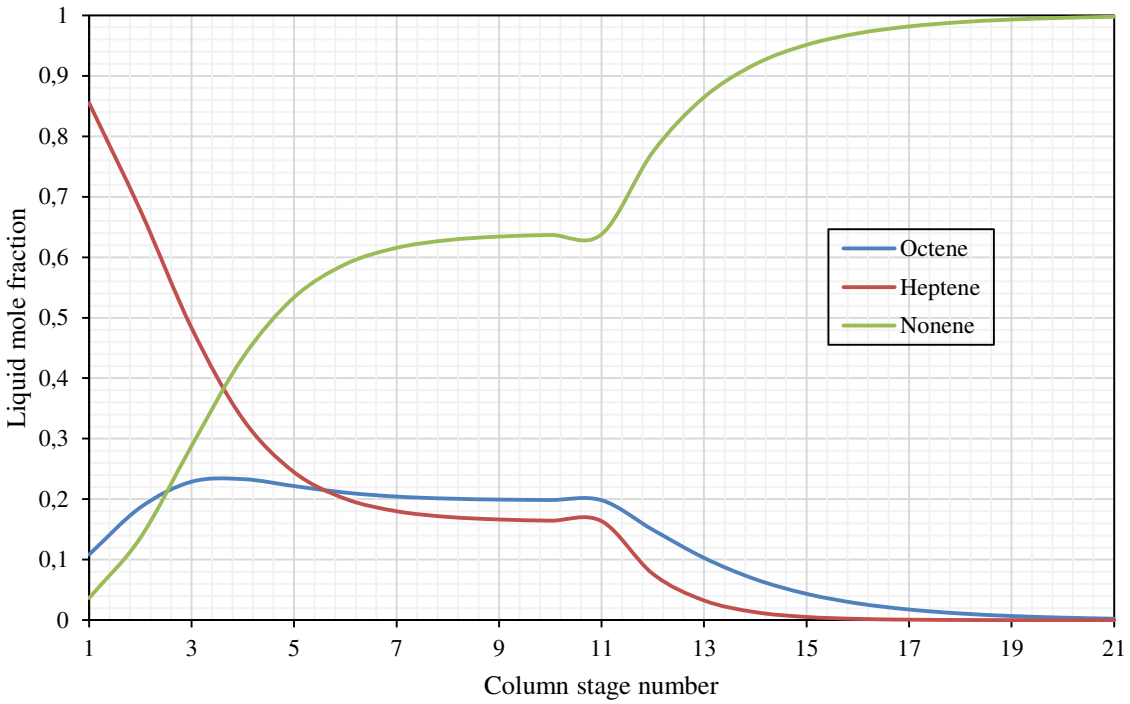

Figure-12. Composition profile of the column for a reflux ratio of 2 and a reboiler duty of 0.3 kJ/s.

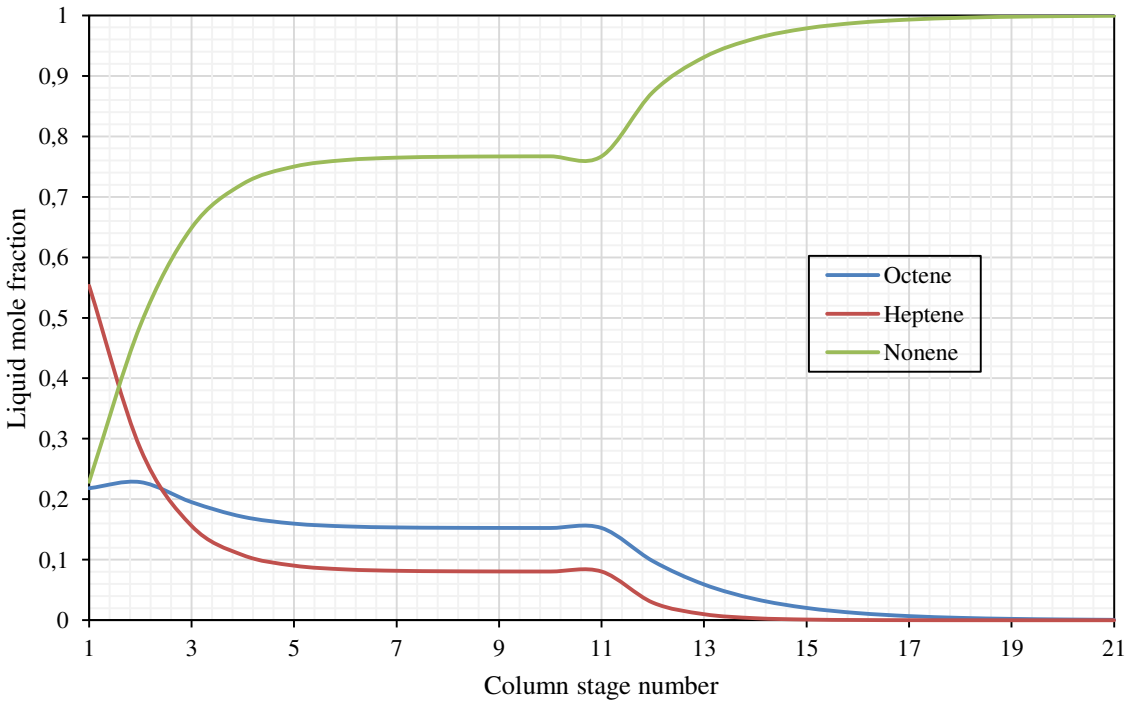

Figure-13. Composition profile of the column for a reflux ratio of 2 and a reboiler duty of 0.4 kJ/s.

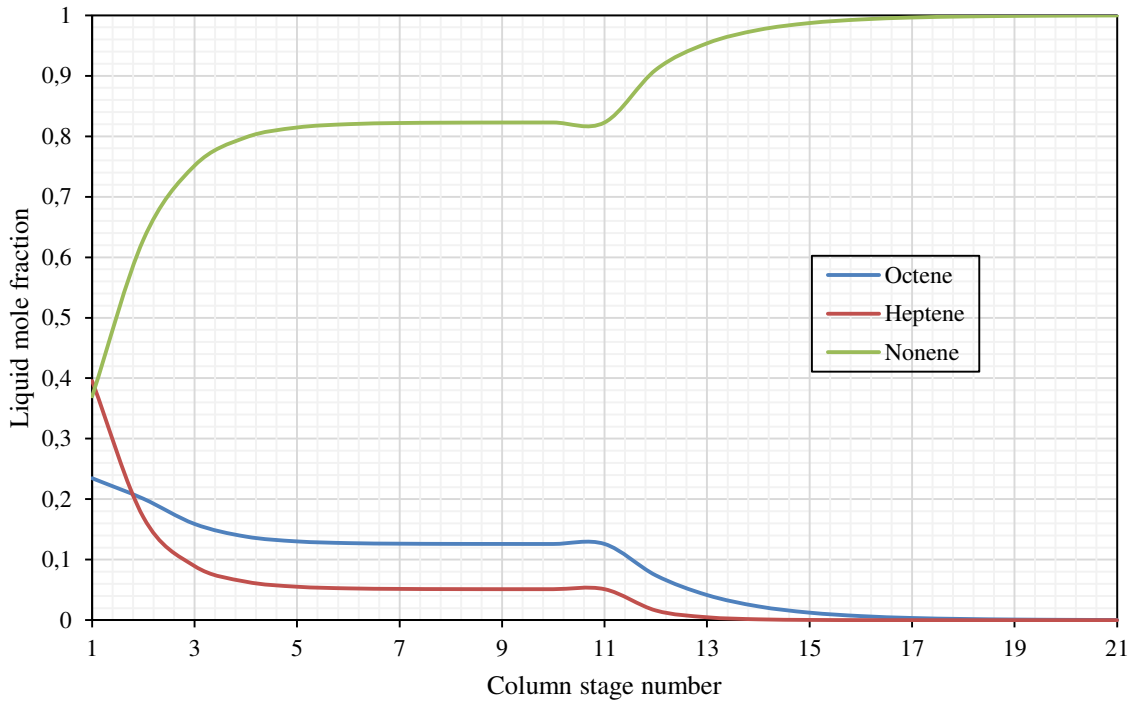

Figure-14. Composition profile of the column for a reflux ratio of 2 and a reboiler duty of 0.5 kJ/s.

Figures 13 and 14 show the composition profiles of the column when the reboiler duty was varied to 0.4 and 0.5 kJ/s respectively with the reflux ratio kept constant at 2. It was discovered from the results that the increase in the reboiler duty of the column gave rise to a mole fraction of nonene obtained from the bottom section of the column to be moving towards unity (1). In other words, as the reboiler duty was being increased, the mole fraction of nonene given by the process at the bottom section of the column was increasing. Considering the response of the mole fraction of heptene given at the top section of the column, it was discovered that there was a kind of inverse proportional relationship in that case because the increase in the reboiler duty was found to result in decrease in the mole fraction of heptene product coming out of the top section of the column.

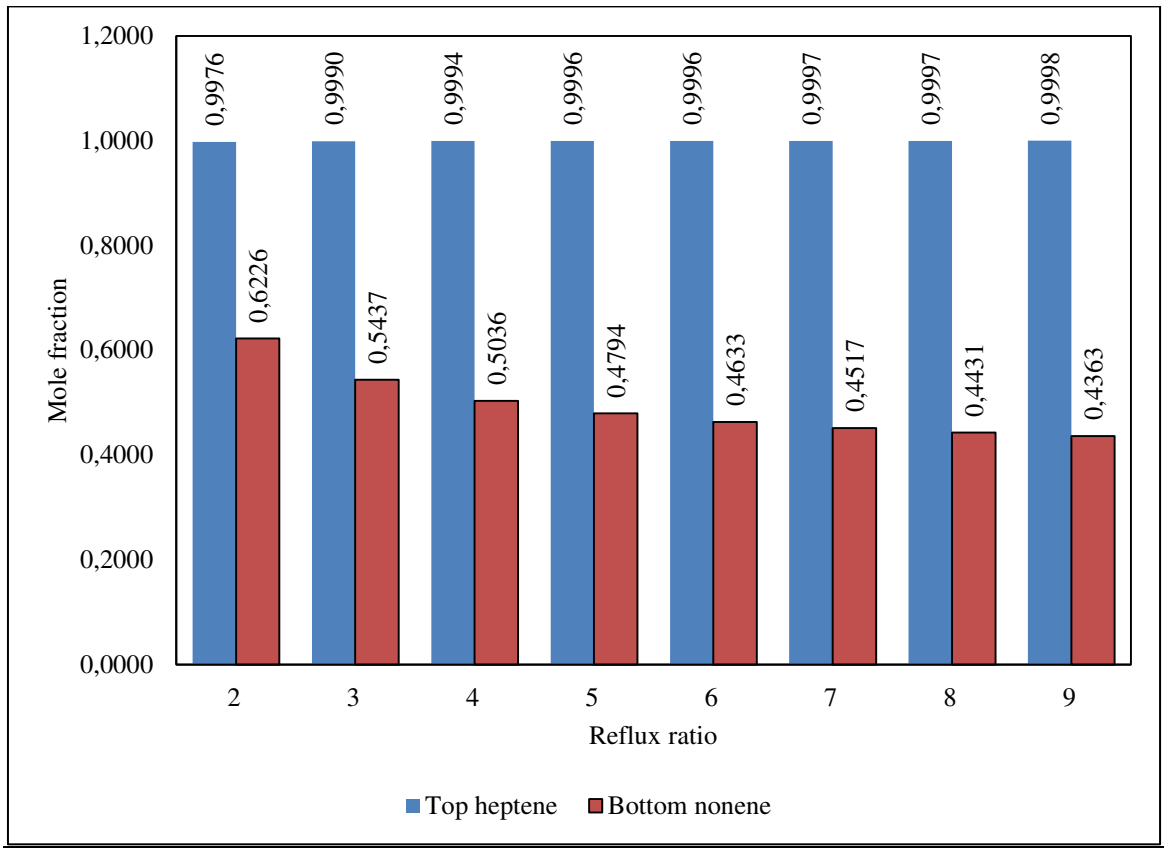

Figure-15. Comparison of heptene and nonene mole fraction obtained from the process at a constant reboiler duty and varying reflux ratio.

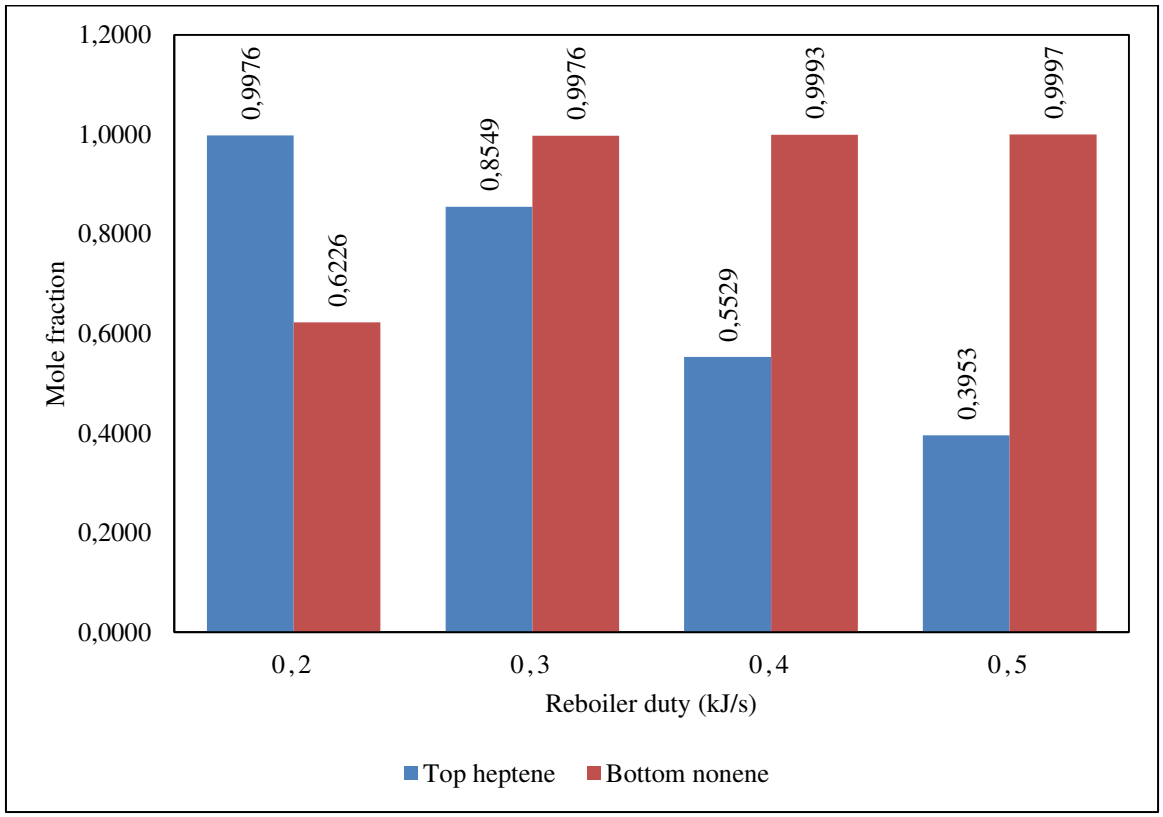

Figure-16. Comparison of heptene and nonene mole fraction obtained from the process at a constant reflux ratio and varying reboiler duty.

Shown in Figure-15 is the comparison between the heptene and the nonene products obtained from the top and bottom sections, respectively of the column when the reflux ratio was varied from 2 to 9. It can be observed from the figure that as the reflux ratio was increased from 2 to 9, the mole fraction of heptene being collected from the top section of the column was approaching one (1) while that of nonene given from the bottom section of the column was decreasing. The reason for this phenomenon was observed to be due to the fact that the purity of the top product, which was heptene, was favoured by the increase in the reflux ratio at the expense of the bottom product, which was nonene that was expected to be collected at the bottom section of the column.

Also given in Figure-16 is the comparison between the top heptene and the bottom nonene given by the process as a result of the variation in the reboiler duty of the column from 0.2 to 0.5 kJ/s. According to the results shown in the figure, the mole fractions of the top heptene was found to decrease while that of the bottom nonene was observed to move towards one as the reboiler duty was varied upwards. The reason for the phenomena occurring in this case was attributed to the fact the formation of bottom product (nonene) was being favoured by the reboiler duty that was the input variable at the bottom section of the column from where the nonene was being collected.

4. CONCLUSIONS

The results obtained from simulation of the octene metathesis reactive distillation process carried out with the aid of ChemCAD for monothetic analysisshowed that the process was affected by both reflux ratio and reboiler duty. It was also discovered from the simulations that the increase in the reflux ratio made the mole fraction of heptene obtained from the top section of the column to approach one while that of the nonene product given from the bottom section of the column was decreasing. Furthermore, the simulations carried out by varying the reboiler duty showed that the increase in the reboiler duty was able to make the mole fraction of the nonene collected from the bottom section of the column to approach one whereas that of the top heptene was found decreasing. The monothetic analysis of this metathesis reactive distillation process has, therefore, revealed that the quality of the products obtained from the top and the bottom sections of the column are dependent upon the values of the reflux ratio and the reboiler duty of the column used.

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